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KINETICS OF CURING REACTIONS FOR EPOXY-AMINE/POLYETHERSULPHONE RESINS

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Differential scanning calorimetry (DSC) was used to indicate the relative extents of the different cure reactions of the 4-glycidyloxyl-N, N-diglycidylaniline (MY0510), polyglycidyl ether of phenol formaldehyde novolac (DEN431) and 3,3 diamino diphenylsulphone (3,3 DDS) resin systems and how these were affected by the presence of polyethersulphone (PES). The extent of reactions at any given time decreased with increasing PES concentration and the reaction rate maximum shifted to longer times. The cured resin systems were examined using dynamic mechanical analysis (DMA). Broader β-transitions of lower intensities were observed in specimens containing PES, suggesting an increased range of relaxations within the transition.

Keywords: DMA, DSC, epoxy-amine/polyethersulphone, kinetics

Introduction

The load carrying integrity of advanced polymer composites is predominantly governed by their toughness and damage tolerance. Although widely used throughout the aerospace and related industries, epoxy based composites are vulnerable due to the inherent brittleness of the epoxy resin. Toughening by blending with a high performance engineering thermoplastic is one approach to reducing this vulnerability. The successful exploitation of such systems requires an evaluation of their processability and end-use behaviour. Understanding of the mechanisms and kinetics of cure and their relation to network morphology are the first essential steps in this process.

It is now generally accepted that in amine cured epoxy resins the primary amine-epoxide addition reaction starts first and proceeds fastest [1–3]. Other possible reactions include secondary amine-epoxide, hydroxyl-epoxide and epoxide-

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epoxide reactions, although there is little agreement in the literature with respect to the relative rates and importance of these within the curing process. The addition of modifiers to epoxy resins to improve their performance is now commonplace [4–6], but little has been published regarding the effect of modifiers on the curing process and resultant network morphology. The most common approach of quantifying the effect of modifiers on the curing process has been to measure heats of reaction, ΔH and the kinetic parameters relative to the neat thermosetting resin system [7]. Differences between the two were then attributed to the contribution made by the modifier to the curing process. The various cure reactions associated with the cure of a typical epoxy-amine have been further investigated through their contribution to the resultant polymer network structure [8]. The shape, height, width and position of the β-transition in dynamic mechanical analysis have been found to reflect contributions made by the various cure reactions to network structure [8–10]. However, for the modified systems the picture is much more complex as a result of the phase relationships between the epoxy and modified phases which may obscure other information. This study thus looks at the effect of polyethersulphone (PES) on the curing behaviour of 4-glycidyloxyl-N, N-diglycidylaniline (MY0510), polyglycidyl ether of phenol formaldehyde novolac (DEN431) and 3,3 diamino diphenylsulphone (3,3 DDS) epoxy-amine polymer system and on the resultant cured polymer network.

Experimental

The 4-glycidyloxyl-N, N-diglycidylaniline (MY0510), polyglycidyl ether of phenol formaldehyde novolac (DEN431) resin system was prepared at a series of 3,3 diamino diphenylsulphone (3,3 DDS) concentrations in the range of 0.8 to 1.3 times the stoichiometric value required for complete cure. Modified epoxy systems were prepared by incorporating hydroxyl terminated polyethersulphone (PES) of various quantities between 0–30%w/w. PES powder was initially dissolved in a 10% mixture of methanol and dichloromethane at 90°C. The resins and curing agent were then added and mixed for 20 minutes. The mixtures was degassed at 120°C (145°C for PES modified systems) and cured at 180°C for 3 hours.

A DuPont DSC 10 was used to quantify the cure kinetics of the epoxy-amine and PES modified systems. The DSC cell was preheated to the desired isothermal temperature and upon reaching thermal equilibrium, opened and the sample in a volatile sample pan (approximately 10 mg), put in place. Runs were allowed to proceed when the cell lid and cover were replaced. Isothermal scans were made at temperature of 145°, 150°, 155°, 160°, 165°, 170°, 180°, 190°, 200° and 210°C. Upon the completion of isothermal scans samples were cooled rapidly to 90°C in the DSC and then heated at 10 deg·min^{-1} to 325°C to determine the residual heat of reaction. The sum of the isothermal and residual heats of cure were taken to represent the ultimate heat of cure.

Dynamic mechanical measurements were conducted using a DuPont Dynamic Mechanical Analyzer (DMA 983). Cured samples of 50 mm length, 10 mm width and 1–3 mm thickness were clamped to a torque value of 10 inch pounds. Clamping distances ranged from 8–20 mm depending on the stiffness/thickness of the specimens. All samples were analyzed in the resonant mode with oscillation amplitudes in the range of 0.45–1.0 mm. The dynamic mechanical properties were recorded in the temperature range –90° to 265°C at a heating rate of 4 deg·min^{-1} to room temperature and 2 deg·min^{-1} above it.

Results and discussion

Figure 1 shows the isothermal results obtained for the 1.05 DDS content epoxy-amine-PES system at a series of temperatures. The material exhibits autocatalysed behaviour as indicated by the non-instantaneous occurrence of the maximum heat flow. The isothermal data was analysed using the DuPont isothermal kinetics software. The program generates 25 partial heat areas at various times to determine the degree of conversion, c, and the corresponding heat flow dH/dt. These are then used to calculate the reaction rate, dc/dt as a function of cure time at each isothermal temperature. The kinetic parameters were calculated using an autocatalysed kinetics model:

$$dc/dt = kc^{m}(1 - c)^{n}$$

where, $k = Ze^{-E/RT}$, Z is the pre-exponential factor, E the activation energy and m and n are reaction orders.

Increases in temperature and DDS concentration increased the extent of reaction at any given time whereas increases in PES decreased it. Plots of the extent of reaction as a function of log time, Fig. 2, showed constant slopes in the intermediate range of conversion for all epoxy-amine formulations at isothermal temperatures in the range of 145°–180°C. Above 180°C, Fig. 3 a gradual increase in the slope was observed with increasing temperature. Formulations containing PES displayed similar effects, but with a shift to longer times. These observations suggest a change in cure mechanism at temperatures above 180°C and that the same overall cure mechanism prevails in both epoxy-amine and epoxy-amine-PES systems although the rate and extent of the curing reactions are decreased in the presence of PES. Figure 4 shows the extent of cure at the peak reaction rate, c_p, as a function of cure temperature for the 0.8 DDS content MY0510-DEN431 system at 0, 10, 20 and 30%w/w PES concentrations. These results indicate that regardless of PES concentration the extent of cure at the maximum rate of reaction is dependent on the cure temperature, particularly at higher temperatures (>170°C) and decreases with increasing temperature. The maximum reaction

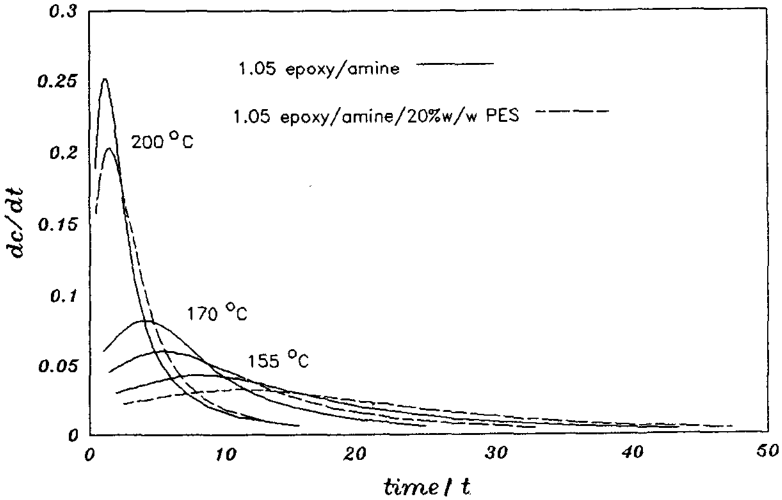

Fig. 1 Reaction rate as a function of time at various temperatures (°C) for the 1.05 DDS MY0510-DEN431 and 1.05 DDS MY0510-DEN431-PES resin systems

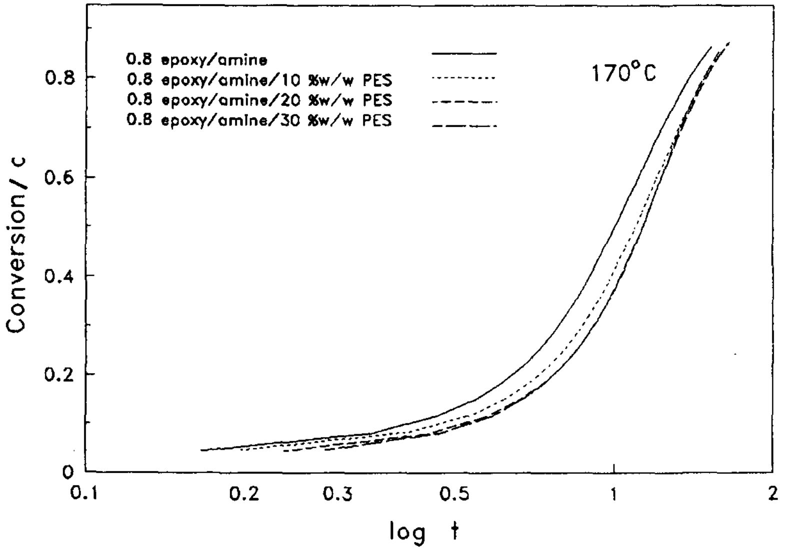

Fig. 2 Conversion (c) as a function of log time 170°C for the 0.8 DDS MY0510-DEN431-PES resin system at 0, 10, 20 and 30%w/w PES

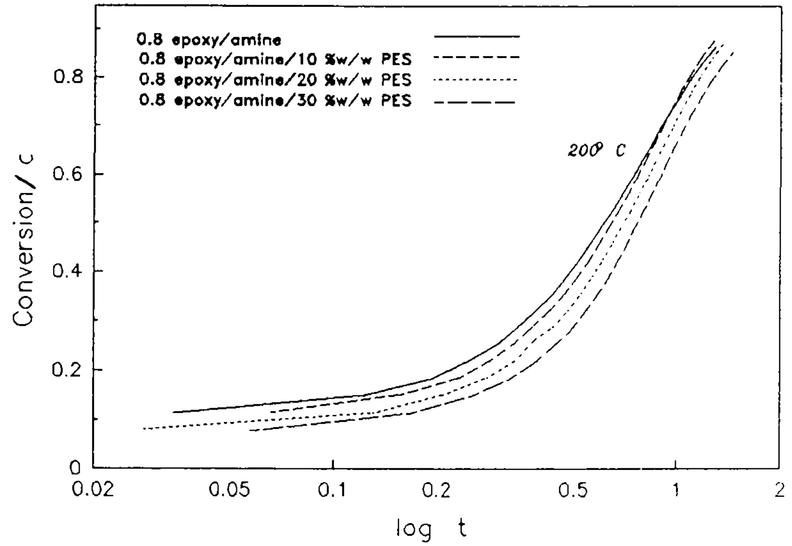

Fig. 3 Conversion (c) as a function of log time at 200°C for the 0.8 DDS MY0510-DEN431-PES resin system at 0, 10, 20 and 30%w/w PES

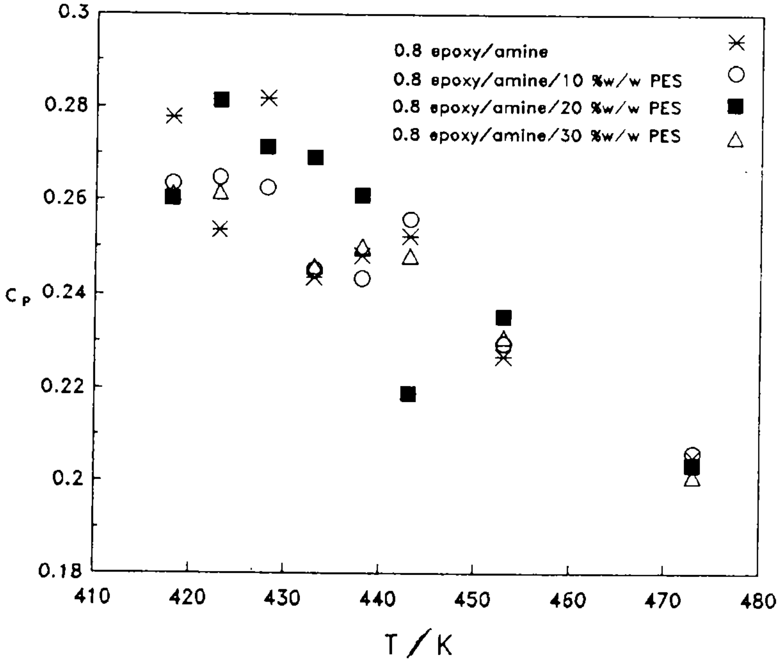

Fig. 4 Extent of reaction at the peak as a function of curing temperature for the 0.8 DDS MY0510-DEN431-PES resin system at 0, 10, 20 and 30%w/w PES

rates in the PES containing formulations occurred at conversions between 19–32%, depending on PES concentration and temperature, compared to 21–34% for the equivalent epoxy-amine systems. This further supports the contention that PES hinders the epoxy-amine curing reaction. Further evidence for a change in the curing mechanism at higher temperatures was observed in plots of time to reach peak temperature, t_p, and the reaction rate constant, *k vs. t*emperature. Figure 5 shows that, above a certain temperature (~ 170°C), *k* exhibited a greater sensitivity to temperature variation. The two distinct trends for the temperature dependence of the reaction rate constant for epoxy-amine and epoxy-amine-PES systems (Fig. 5) each satisfy the classical Arrhenius form although there is some deviation at the highest temperatures. Values of the reaction order m were calculated using the isothermal kinetics software. For all formulations, the value of *m* (0.3 to 1.2) decreased with increasing cure temperature and PES concentration, Fig. 6. Plots of reaction rate *vs.* the extent of reaction (Fig. 7), for the 0.8, 30%w/w epoxy-amine-PES systems showed the appearance of a second exotherm, peaking at approximately 40% conversion. Similar features were observed for the 1.05 epoxy-amine-PES system. The exotherm was most prominent at high temperatures and/or PES concentrations, but diminished by increasing amine content. Unfortunately the overlap of exotherms hindered their isolation and quantitative analysis. These observations contrast with epoxy-amine systems which showed no evidence of a second exotherm. From the results obtained it can be hypothesized that although the epoxy-amine addition reactions are the

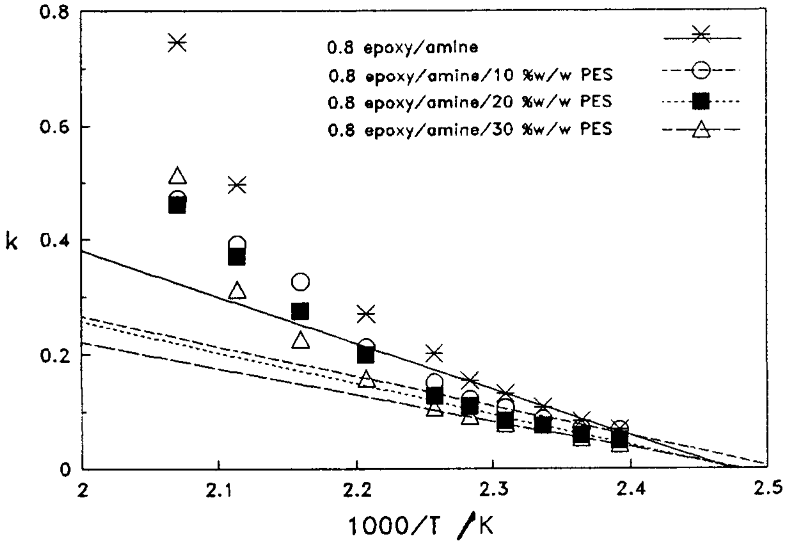

Fig. 5 Reaction rate constant *k* as a function of temperature for the 0.8 DDS MY0510-DEN431-PES resin system at 0, 10, 20 and 30%w/w PES

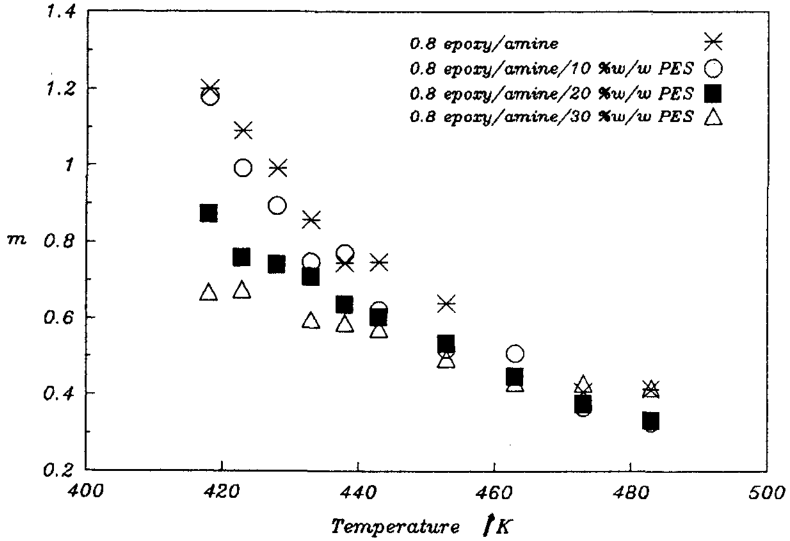

Fig. 6 Reaction order *m* as a function of curing temperature for the 0.8 DDS MY0510-DEN431-PES resin system at 0, 10, 20 and 30%w/w PES

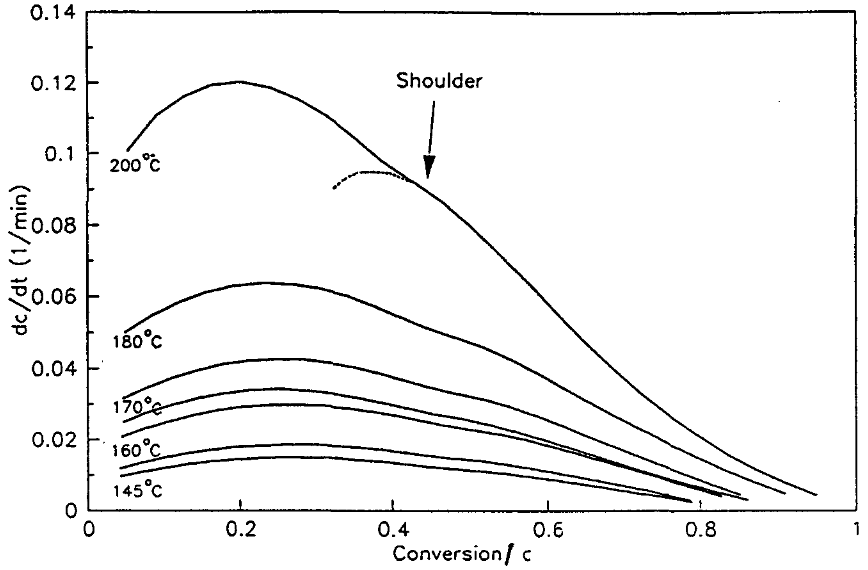

Fig. 7 Reaction rate as a function of conversion at various temperatures for the 0.8 DDS MY0510-DEN431-PES resin system at 30%w/w PES

dominant cure reactions it is likely that the apparent change in mechanism observed at high temperatures and low DDS concentrations (results not presented here for brevity) emphasis the role of the epoxy-hydroxyl (E–OH) reaction. The resolution of the second exotherm in PES systems at high temperatures and PES concentrations and low amine concentrations thus suggest PES further activates the E–OH reaction. Steric and diffusional limitations imposed by PES on the formation of the epoxy-amine network during cure would almost certainly restrict the amount of interaction between PES and epoxy and account for the decrease of reaction rate with increasing PES concentration. This is further supported by the diminishing of the secondary exotherm at lower temperatures and higher DDS concentrations where there is less available epoxide and the epoxide-amine addition reactions are more dominant. The relative extents of the various cure reactions were further examined by dynamic mechanical analysis. β-relaxation transition, indicated at –33° to –8°C in tan δ plots, were found to be sensitive to variations in the amine concentration of the epoxy-amine systems and to variations in the PES content of the epoxy-amine/thermoplastic blends. Increasing the amine concentration corresponded to increases in the height and decreases in the width of the relaxation, whereas in the blends the β-transition decreased in height and increased in width as shown in Fig. 8, indicating a greater range of molecular relaxations at transition. This is attributed to the notion that PES depresses epoxide-amine reaction and promotes E–OH reactions.

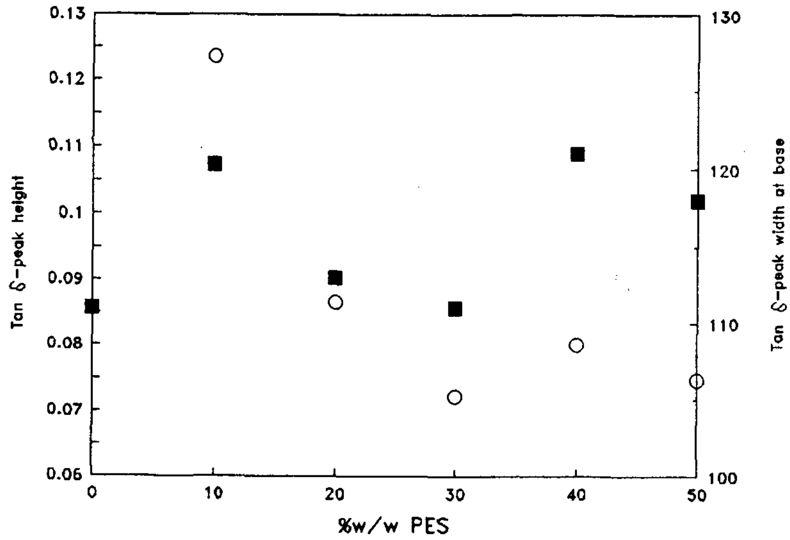

Fig. 8 β-transition peak height o and peak width at base ■ at various PES concentration for the 0.8 DDS MY0510-DEN431-PES resin system

Conclusion

a) Isothermal differential scanning calorimetry (DSC) analysis show that the epoxy-amine systems and the blends of these epoxies with polyethersulphone (PES) demonstrate an autocatalytic curing behaviour. The rate and extent of reaction at any given time increases with increasing cure temperature and/or amine content, and decreases with increasing PES concentration. These variations, in turn, yield different reaction-rate constants, k and reaction rate orders, m and n for the autocatalytic kinetics model.

b) Epoxy-amine/PES blends exhibit a second exotherm during the isothermal DSC runs, the intensity of which diminishes with increasing amine content and augments with increasing cure temperature and/or PES content.

c) The β-relaxation transition, occurring at –33° to –8°C in tan δ traces, is also found to be sensitive to variations in the amine and PES contents. Increasing the amine concentration in epoxides results in sharper peaks of greater intensities, whereas the incorporation of PES generates broader and more shallow peaks.

d) The conclusions (b) and (c) indicate that PES depresses epoxide-amine reactions and possibly promotes the epoxy-OH reaction.

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Zusammenfassung — DSC wurde eingesetzt, um den relativen Anteil der verschiedenen Härtungsreaktionen von 4-Glycidyloxyl-N,N-diglycidylanilin (MY0510), Polyglycidylether von Phenolformaldehyd Novolack (DEN431) und 3,3-Diamino-diphenylsulfon (3,3 DDS) Harzsysteme sowie deren Beeinflussung durch die Gegenwart von Polyethersulfon (PES) zu bestimmen. Der Anteil aller Reaktionen nimmt zu jeder Zeit mit steigender PES Konzentration ab und die maximalen Reaktionsgeschwindigkeiten werden später erreicht. Die gehärteten Harze wurden mittels DMA untersucht. In den PES-haltigen Materialien konnten breitere ß-Übergänge geringer Intensität beobachtet werden, was einen größeren Relaxationsbereich innerhalb des Überganges zeigt.